



# Energy-efficient fabrication of a novel multivalence $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$ heterojunction for dye degradation under visible light irradiation

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## ABSTRACT

A novel  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  valence state heterojunction was fabricated for the first time by a low-temperature hydrothermal method and further applied for methylene blue (MB) degradation under visible light irradiation at room temperature. The  $\text{Mn}_3\text{O}_4$  core with tetragonal hausmannite structure was coated by a thin amorphous  $\text{MnO}_2$  shell. The specific surface area and light-response range of  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  photocatalyst were significantly enhanced by doping  $\text{MnO}_2$ . Noticeably, the  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  exhibited excellent photocatalytic activity with the degradation efficiency of MB up to 93.5% within 1 h. Moreover, the mechanism for MB photocatalytic degradation by  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  was also explored. The superoxide radicals made a major contribution to the photo-degradation process, followed by the photo-induced holes and hydroxyl radicals. The surface oxygen of  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  also took part in the formation of superoxide radicals, which could be replenished by atmospheric oxygen. More importantly, the formation of type II heterojunction in  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  composite could accelerate the spatial separation of photo-induced carriers. This novel multivalence  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  core-shell composite photocatalyst proved to have great potentials for organic contaminants degradation in water.

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## 1. Introduction

With the development of modern industry, organic compounds such as dyes, pesticides, pharmaceuticals and phthalate esters in environment, especially in water body, have been detected frequently [1–3]. Researches have reported that these organic compounds are posing serious threats to human health and environmental sustainability due to their toxicity and persistence, which has aroused great concern worldwide [4–6].

Conventional water treatment processes including biodegradation and adsorption can remove most organic compounds from wastewater. Nevertheless, the biodegradation process is relatively slow and ineffective for treatment of toxic organics due to the sensitivity of organisms [7]. Although these pollutants can be transferred from polluted water to solid by adsorption technology, they still need further treatment [8]. Alternatively, advanced oxidation technology can degrade refractory organic pollutants from water thoroughly, reducing the harm to the environment and human

body fundamentally [9]. Among them, photocatalytic oxidation technology is believed to be the most green and promising strategy for contaminants removal because of the solar energy utilization and no additional oxidants [10,11]. As is known that the catalyst properties such as light-harvesting efficiency, band gap structure and surface area play important roles in photocatalytic activity. Thus, designing and developing a novel photocatalyst with high-efficiency should be a key point to solve the problem of organic pollution in water.

Various types of photocatalysts have been fabricated ranging from one-component of titanium dioxide ( $\text{TiO}_2$ ), zinc oxide ( $\text{ZnO}$ ), stannic oxide ( $\text{SnO}_2$ ), tungsten trioxide ( $\text{WO}_3$ ) and graphite carbon nitride ( $\text{g-C}_3\text{N}_4$ ) to multi-components of  $\text{TiO}_2$ - and  $\text{ZnO}$ -based composites, silver- and bismuth-based compounds and so on [11–17]. As for the one-component photocatalysts, most of them had strong absorption in the ultraviolet range, while the absorption of visible light was low, being unable to make full use of the solar energy and declining their industrial values. Besides, the fast recombination of the photo-generated electrons and holes decreases their photocatalytic efficiency [18]. Although the multicomponent photocatalysts have enhanced the photocatalytic performance to some extent by extending the absorption region and prolonging the lifetime of carriers, the transfer process of photo carriers between

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the bands of photocatalysts with different elements may cause energy loss, weakening their oxidation ability [18,19]. Recent studies have demonstrated that carriers and energy could be transferred facilely between different valence states of an element, which was beneficial to photocatalytic reactions [20–22]. As a green and bountiful resource, manganese with multivalence states (+2, +3, +4, +6 and +7) has attracted growing attentions in the photocatalytic field because they could be sensitized by visible light [22–24]. Lately,  $\text{Mn}_3\text{O}_4/\text{MnCO}_3$  valence state heterojunction was successfully fabricated, which could degrade methylene blue (MB) and formaldehyde (CHOH) efficiently under synergistic effect of photo and thermal at high temperature (80 °C) [22]. However, the broad band gap of  $\text{Mn}_3\text{O}_4$  (2.3 eV) and  $\text{MnCO}_3$  (5.0 eV) made them not fully utilize the whole visible light. More importantly, the whole process seemed to be energy-consuming because large amount of heat energy was needed not only in the preparation process but also in the reaction process.

Manganese dioxide ( $\text{MnO}_2$ ), with a narrow bandgap and high surface area, could increase the utilization rate of visible light, which have significantly improved the photocatalytic performance of  $\text{TiO}_2$  [25], bismuth oxyiodide ( $\text{BiOI}$ ) [26] and mesoporous silica [27] under visible light irradiation. Manganous manganic oxide ( $\text{Mn}_3\text{O}_4$ ) as a low-cost p-type semiconductor was also applied to promote the photocatalytic performance of composite photocatalysts [24]. The combination of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  would provide valuable advantages such as strong visible light absorption, more active sites and enhanced charge separation performance. Herein, the mixed-valent  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  heterojunction was fabricated for the first time by a facile and energy-effective method through a hydrothermal process at 363 K. The inexpensive  $\text{MnCl}_2$  and  $\text{KMnO}_4$  were applied as precursors of manganese element and no additional oxidizer or reductant was added in the synthetic process. The visible light absorption of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  was dramatically enhanced, achieving highly MB degradation in visible light. The recombination of photo-carriers was limited effectively by the formation of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  heterojunction. Moreover, the major active species in the photocatalytic process were also identified. This novel  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell composite would enjoy bright prospect in photo-degradation of organic pollutants in water.

## 2. Experimental

### 2.1. Chemicals

All chemicals used in this study were analytical grade. Besides, deionized (DI) water was applied as solvent. Manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ), potassium permanganate ( $\text{KMnO}_4$ ) and sodium hydroxide ( $\text{NaOH}$ ) were supplied by Xilong Chemical Co., Ltd (Shantou, China) while Poly (vinylpyrrolidone) (PVP, K-30) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

### 2.2. Synthesis

The photocatalysts were fabricated with a low-temperature hydrothermal method at 363 K under continuous stirring. The specific operations were as follows.

#### 2.2.1. Synthesis of $\text{Mn}_3\text{O}_4$ nanoparticles

The DI water (80 mL) in a glass bottle was heated to 363 K. Then 20 mL solution containing 4.5 mmol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.0 g PVP was added to the glass bottle. After that, 4.5 mL  $\text{NaOH}$  (2.0 M) was immediately added to the mixture, producing light brown precipitate. The precipitate was aged in mother solution for 3 h under stirring. After the solution cooled to room temperature, the solid powder was separated by centrifugation and was washed three times with

DI water and ethanol, respectively. Finally, it was dried at 353 K in a vacuum drying oven.

#### 2.2.2. Synthesis of $\text{Mn}_3\text{O}_4\text{-MnO}_2$ nanosheets

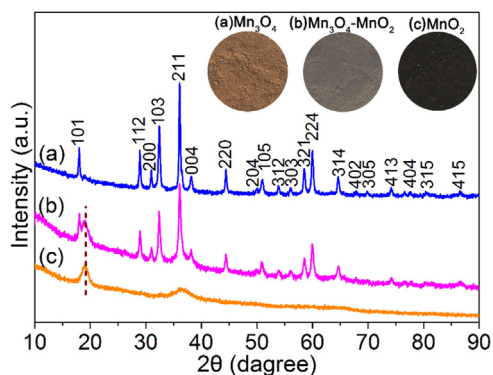
The  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite with molar ratio of  $\text{Mn}_3\text{O}_4:\text{MnO}_2 = 2:5$  was fabricated. The DI water (80 mL) in a glass bottle was heated to 363 K. Then 20 mL solution containing 4.5 mmol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.0 g PVP was added to the glass bottle. After that, 4.5 mL  $\text{NaOH}$  (2.0 M) was immediately added to the bottle, producing light brown precipitate. About 2 min later, 5.0 mL of 0.2 M  $\text{KMnO}_4$  solution was added into the mixture and kept stirring for 3 h. The separation, washing and drying operations for  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite were the same as those for  $\text{Mn}_3\text{O}_4$  nanoparticles. The  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composites with molar ratios of 3:5 and 1:5 were also fabricated by adjusting the molar ratios of  $\text{MnCl}_2$  and  $\text{KMnO}_4$ . The samples were characterized by X-ray diffraction (XRD, Fig. S1), shown in the Supporting information. The composite  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  with ratio of  $\text{Mn}_3\text{O}_4:\text{MnO}_2 = 2:5$  exhibited excellent photocatalytic activity (presented in Fig. S2), which was mainly investigated and reported in this paper.

#### 2.2.3. Synthesis of $\text{MnO}_2$ nanoplates

The 4.5 mmol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.0 g PVP were dissolved in 20 mL DI water. Then the solution was added to 80 mL DI water in a glass bottle which had been heated to 363 K using the heating stirrer. After that, 4.5 mL  $\text{NaOH}$  (2.0 M) was added to the glass bottle immediately. About 2 min later, 9.0 mL of 0.2 M  $\text{KMnO}_4$  solution was added into the mixture and kept stirring for 3 h. The separation, washing and drying operations for  $\text{MnO}_2$  nanoplates were the same as those for  $\text{Mn}_3\text{O}_4$  nanoparticles.

### 2.3. Characterization

XRD patterns of the prepared samples were obtained using a diffractometer (Empyrean, Panalytical, Netherlands) equipped with  $\text{Cu K}\alpha$  radiation. The chemical species of the samples were analyzed by X-ray photoelectron spectroscopy (XPS; Escalab 250Xi, Thermo Fisher Scientific, US) and all binding energies of the elements were calibrated referring to the  $\text{C1s}$  peak at 284.8 eV of adventitious carbon. Surface morphology of the samples was examined by a field-emission scanning electron microscopy (FESEM, HELIOS NanoLab 600i, US) after spraying a thin gold layer. Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HRTEM) images, selected-area electron diffraction (SAED) patterns and electron energy loss (EEL) spectra of the samples were acquired by a field-emission transmission electron microscopy (FETEM, Tecnai G2 F30, US) with an electron energy loss spectroscopy (EELS) analyzer. The samples were also examined by Fourier transform infrared spectrometer (FTIR, Perkin Elmer, US) with scan range from 400 to  $4000\text{ cm}^{-1}$  after pressing into tablets with KBr powder. The specific surface area of the samples were determined by the Brunauer-Emmett-Teller (BET) method at 77 K with an ASAP 2020 system (Quantachrome, US). Ultraviolet-visible (UV-vis) diffuse reflectance spectra was measured by the spectrophotometer (UV 2550, Shimadzu, Japan) with  $\text{BaSO}_4$  as reference. The transient photocurrent response and electrochemical impedance spectroscopy (EIS) of the samples were measured in a three-electrode quartz cell in 0.1 M  $\text{Na}_2\text{SO}_4$  electrolyte by an electrochemical work station (CHI-660B, China). The platinum (Pt) electrode and calomel electrode were worked as counter and reference electrodes, respectively. The indium-tin oxide (ITO) electrode coated with photocatalyst was used as the working electrode. The visible light was applied by a 300 W Xe lamp.



**Fig. 1.** XRD patterns of (a)  $\text{Mn}_3\text{O}_4$ , (b)  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and (c)  $\text{MnO}_2$ . The insets were photographic images of  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  powders.

#### 2.4. Photocatalytic reaction

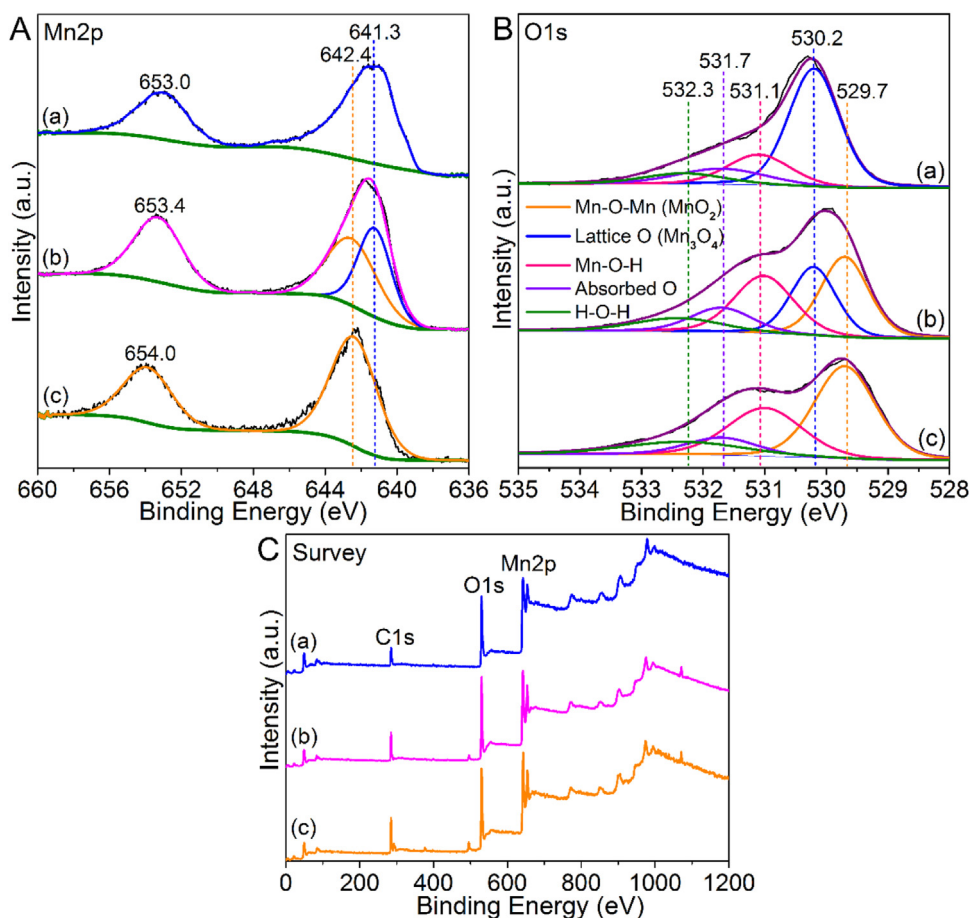
The photocatalytic reactions were carried out in a 200 mL quartz beaker with 100 mL methylene blue (MB) solution at room temperature. The initial MB concentration was 10 mg/L and the catalyst dosage was determined as 0.5 g/L (Fig. S3). In the first 30 min, the suspensions were kept stirring in dark to reach adsorption-desorption equilibrium (Fig. S4). Then the MB solutions were degraded under visible light ( $\lambda > 420$  nm) provided by a 300 W Xe lamp (NBET Technology Co., Ltd, China) equipped with two cutoff filters (UVCUT 400 and VisREF 780). The distance between the light source and the samples was 10 cm. At given time intervals, about 3.0 mL MB suspension was withdrawn by a pipette. After centrifugation,

the solution concentrations were measured at 664 nm by an UV-vis spectrophotometer (T9, Persee, China). The reusability of the newly-fabricated composite catalyst was investigated by recycling the photo-degradation of MB. The separated photocatalyst was irradiated under visible light for 30 min to remove the adsorbed MB before the next photo-degradation experiment. Besides, the residual concentration of manganese in solution was measured by an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer Optima, US).

### 3. Results and discussion

#### 3.1. Phase constitution and morphology of photocatalysts

The structures of the three as-prepared products were examined by X-ray diffraction (XRD) technique and the results were shown in Fig. 1. All the diffraction peaks in Fig. 1(a) were perfectly indexed to  $\text{Mn}_3\text{O}_4$  with tetragonal hausmannite structure (space group:  $I4_1/amd$ ,  $a = 5.763$  Å,  $c = 9.471$  Å, JCPDS NO. 24-0734) and no any other crystalline peaks was detected. Similarly, the diffraction peaks of tetragonal  $\text{Mn}_3\text{O}_4$  were also observed in Fig. 1(b). Besides, a broad peak located at  $2\theta = 19.2^\circ$  appeared, which was identified as amorphous  $\text{MnO}_2$  [28]. The composite photocatalyst fabricated in this study was constituted of crystalline  $\text{Mn}_3\text{O}_4$  and amorphous  $\text{MnO}_2$ . As shown in Fig. 1(c), two broad peaks at  $19.2^\circ$  and  $37.0^\circ$  were observed clearly, which were indexed to  $\alpha\text{-MnO}_2$  (JCPDS No. 44-0141) with amorphous state [29]. In the insets, the color of the fabricated  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  powders were brown, dark brown and black, respectively.



**Fig. 2.** The XPS spectra of (a)  $\text{Mn}_3\text{O}_4$ , (b)  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and (c)  $\text{MnO}_2$ : (A) Mn 2p, (B) O 1s and (C) survey scan.

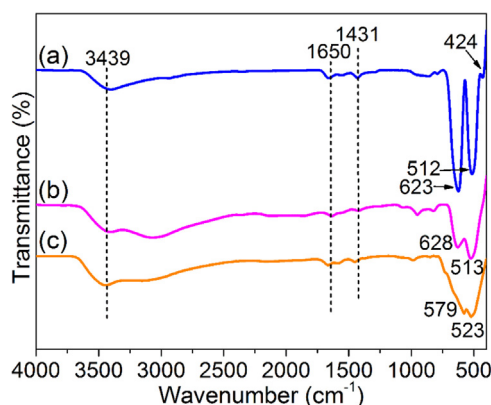


Fig. 3. FT-IR spectra of (a)  $\text{Mn}_3\text{O}_4$ , (b)  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and (c)  $\text{MnO}_2$ .

To further determine the chemical composition of the photocatalysts, X-ray photoelectron spectroscopy (XPS) measurement was carried out. The XPS survey scan of the three photocatalysts were supplied in Fig. 2C, which showed the characteristic peaks of manganese (Mn), oxygen (O) and adventitious carbon (C). The high-resolution Mn 2p and O 1s spectra were presented in Fig. 2A and B, respectively. As shown in Fig. 2A, the peaks of Mn 2p<sub>3/2</sub> were located at binding energy (BE) of 641.3 and 642.4 eV, which were consistent with the reported values of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  [28,30]. Thus the catalysts shown in Fig. 2A (a) and (c) were confirmed as pure  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$ . The Mn 2p<sub>3/2</sub> spectrum in Fig. 2A (b) demonstrated that the composite catalyst was composed of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$ , including multivalent state manganese ( $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ ). It was also obtained from XPS analysis that the Mn content in  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  for the composite were 54.23% and 45.77% respectively, indicating the ratio of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  in the composite was about 2:5. Such a conclusion was further validated by the XPS results of O 1s. As shown in Fig. 2B, the BE values of approximately 529.7, 530.2, 531.1, 531.7 and 532.3 eV were corresponded to the bulk oxygen of  $\text{MnO}_2$ , lattice oxygen of  $\text{Mn}_3\text{O}_4$ , surface hydroxyl bonded to Mn, absorbed oxygen and adsorbed molecular water, respectively [22,30,31]. The corresponding oxygen species in  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite (Fig. 2B (b)) accounted for 29.62%, 23.71%, 26.18%, 11.53% and 8.96%, respectively. It was further confirmed that the ratio of  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  in the composite was 2:5. Besides, it should be noted that the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite possessed abundant surface oxygen, which played important roles in photocatalytic reactions [32].

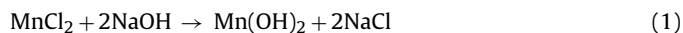
Fourier transformation infrared spectroscopy (FTIR) measurements were performed to further identify the chemical bonds and functional groups in the photocatalysts. The infrared spectra were recorded and presented in Fig. 3. Among these absorption bands, the band around 3439  $\text{cm}^{-1}$  was typically ascribed to the O–H stretching vibration of absorbed water molecules, and the other two bands located at 1650 and 1431  $\text{cm}^{-1}$  were attributed to the bending vibration of hydroxyl combined with Mn atoms [31,33]. Besides, three characteristic absorption bands of  $\text{Mn}_3\text{O}_4$  were observed in Fig. 3(a) with the range of 650–400  $\text{cm}^{-1}$  [30]. The two broad bands at 623 and 512  $\text{cm}^{-1}$  were correspond to the Mn–O stretching vibration in tetrahedral sites and distortion vibration in an octahedral environment, respectively. The band at 424  $\text{cm}^{-1}$  was attributed to the stretching vibration of  $\text{Mn}^{3+}$  in the octahedral sites. As for the spectrum of  $\text{MnO}_2$  in Fig. 3(c), two significant bands at 579 and 523  $\text{cm}^{-1}$  were observed, which were associated with the Mn–O vibrations of  $\text{MnO}_6$  octahedral framework in the  $\text{MnO}_2$  [33]. Furthermore, the two asymmetric vibrations at 528 and 513  $\text{cm}^{-1}$  for  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite in Fig. 3(b) should be

attributed to the vibration superposition of Mn–O in  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$ .

The typical scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  photocatalysts were shown in Fig. 4. As can be seen from Fig. 4(a–b), the morphology of pure  $\text{Mn}_3\text{O}_4$  presented spherical particles with diameters ranging from 60 to 90 nm and the aggregation phenomena between  $\text{Mn}_3\text{O}_4$  nanoparticles was observed. The lattice fringe of 0.493 nm could be clearly seen from the high resolution transmission electron microscopy (HRTEM) image in Fig. 4(c), corresponding to the (101) plane of  $\text{Mn}_3\text{O}_4$ . The SEM image in Fig. 4(d) revealed that the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite exhibited sheet structure with thickness of 20 nm approximately. From the TEM image in Fig. 4(e), it could be inferred that the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite had core-shell structure, which was further identified by the HRTEM image enlarged from the TEM image. As shown in Fig. 4(f), the lattice fringes of 0.309 and 0.249 nm were assigned to the (112) and (211) crystal planes of  $\text{Mn}_3\text{O}_4$ , respectively. Furthermore, the amorphous  $\text{MnO}_2$  at the edge adhered on the  $\text{Mn}_3\text{O}_4$  surface, indicating the core-shell structure of the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  nanosheets. Besides, the core-shell structure was further confirmed by electron energy loss spectroscopy (EELS) analysis (Fig. S5, details were shown in Supporting information). The selected-area electron diffraction (SAED) pattern of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  nanosheets was presented in the inset. The polycrystalline diffraction rings were corresponded to the (101), (112), (103), (211), (220), (105) and (321) planes of tetragonal hausmannite  $\text{Mn}_3\text{O}_4$ . The crystal structure of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  given by the SAED pattern and HRTEM image was consistent with the results obtained by XRD analysis. As shown in Fig. 4(g–i), the pure  $\text{MnO}_2$  presented plate-like morphology and no obvious crystal lattice fringe could be observed from the HRTEM image, revealing its amorphous form.

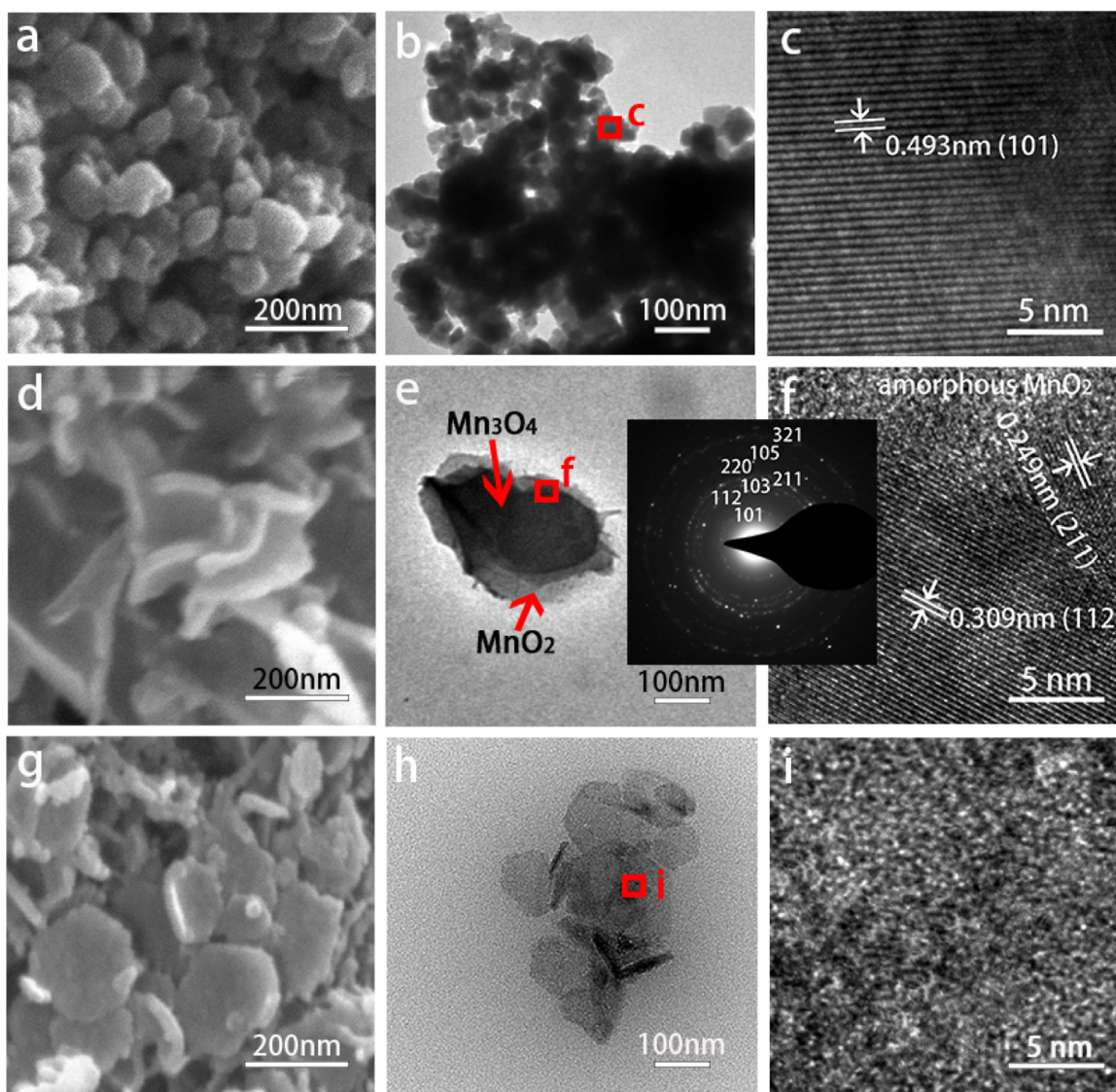
### 3.2. The formation mechanism of photocatalysts

The formation mechanism of  $\text{Mn}_3\text{O}_4$  nanoparticles,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell nanosheets and  $\text{MnO}_2$  nanoplates were proposed based on their composition and stoichiometric relationship. The fabrication processes were illustrated in Fig. 5. The growth mode and ultimate shape of the photocatalysts were directed by Poly (vinyl pyrrolidone) (PVP) [34]. The three photocatalysts shared the same reactions (Eqs. (1) and (2)) during the early prepared stage. When the 9.0 mmol NaOH was added to the mixture containing 4.5 mmol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  and 1.0 g PVP, the white  $\text{Mn}(\text{OH})_2$  precipitate was produced by the reaction between  $\text{MnCl}_2$  and NaOH under stirring. And then a fraction of  $\text{Mn}(\text{OH})_2$  was converted into brown  $\text{MnO}(\text{OH})_2$  under the influence of dissolved oxygen in water [35].



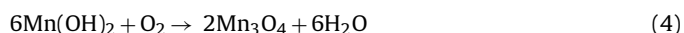
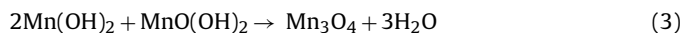
The  $\text{Mn}_3\text{O}_4$  nanoparticles were fabricated without dosage of  $\text{KMnO}_4$  into the system. It was suggested that the redox and dehydration reaction between  $\text{Mn}(\text{OH})_2$  and  $\text{MnO}(\text{OH})_2$  occurred (Eq. (3)). Besides, a part of  $\text{Mn}(\text{OH})_2$  precipitate might react with the dissolved oxygen directly (Eq. (4)). Also, the two reaction equations of Eqs. (2) and (3) can be combined into one equation written as Eq. (4). As is well known, the surface of larger nanoparticles with lower energy was more stable than that of small nanoparticles. The produced seed nucleus of small  $\text{Mn}_3\text{O}_4$  nanoparticles were inclined to growth due to their high surface energy and ferromagnetism [36]. Meanwhile, PVP adsorbed on the surface of  $\text{Mn}_3\text{O}_4$  nanoparticles to restrict their further growth. With the reaction continuing, the small  $\text{Mn}_3\text{O}_4$  nanoparticles were gradually dissolved and contributed to the growth of large nanoparticles. The growth process would be continue until all the small  $\text{Mn}_3\text{O}_4$  nanoparticles were





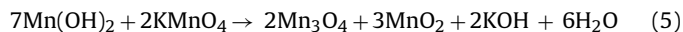
**Fig. 4.** SEM, TEM and HRTEM images of  $\text{Mn}_3\text{O}_4$  (a–c),  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  (d–f) and  $\text{MnO}_2$  (g–i). The inset between (e) and (f) displayed the SAED pattern of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$ .

consumed completely, which was known as Ostwald ripening [34]. Finally, the  $\text{Mn}_3\text{O}_4$  nanoparticles with relatively uniform size were fabricated by an isotropic growth mode.



In order to fabricate the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell photocatalyst, 1.0 mmol  $\text{KMnO}_4$  was added to the reaction system, then the redox reaction between  $\text{Mn}(\text{OH})_2$  and  $\text{KMnO}_4$  took place rapidly with the precipitate color changing from light brown into dark brown (Eq. (5)). In addition, the  $\text{MnO}(\text{OH})_2$  precipitate was turned into  $\text{MnO}_2$  by dehydration reaction (Eq. (6)). Similarly, the formed  $\text{Mn}_3\text{O}_4$  acted as seed nucleus for the further growth of  $\text{Mn}_3\text{O}_4$  nanoparticles. At the same time, the in situ generated  $\text{MnO}_2$  could be adhered on the  $\text{Mn}_3\text{O}_4$  surface by surface hydroxyl radicals, forming a thin shell. As the molar ratio of PVP to manganese source decreased, the coverage of PVP on the faces of the seeds was declined, then the growth mode of the small nanoparticles changed from isotropic growth to anisotropic growth. Generally, the formation of 2-dimensional (2D) structured nanomaterials is attributed to the anisotropic growth along a plane. In this case, one plane of nanoparticles was attached with PVP and the corresponding surface

energy decreased. Then the other plane of the nanoparticles with high surface energy was linked by adjacent nanoparticles. In brief, the relatively lower coverage of PVP on nanoparticles kept them growing along one plane, forming the 2D structured  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell nanosheets through Ostwald ripening.



The reaction process and ultimate products in our reaction system were obviously influenced by the variation of redox conditions. As presented in Eq. (7), with the dosage of  $\text{KMnO}_4$  increasing to 1.8 mmol, the  $\text{MnO}_2$  precipitate was produced immediately through the redox reaction between  $\text{Mn}(\text{OH})_2$  and  $\text{KMnO}_4$ . Besides, the  $\text{MnO}(\text{OH})_2$  precipitate was also converted into  $\text{MnO}_2$  by dehydration reaction (Eq. (6)). The formation mechanism of 2D  $\text{MnO}_2$  nanoplates was similar to that of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  nanosheets. On this occasion, the generated  $\text{MnO}_2$  nanoparticles also showed anisotropic growth mode at the surface covered by PVP incompletely. These small  $\text{MnO}_2$  nanoparticles were bridged together

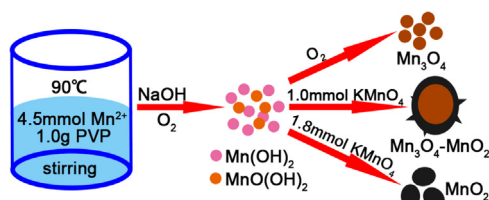
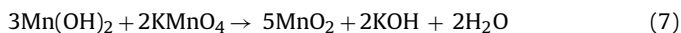


Fig. 5. Schematic illustration of the fabrication processes of  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$ .

along one plane through surface hydroxyl radicals, forming the 2D structured nanoplates by Ostwald ripening process.



### 3.3. Photocatalytic activities

To evaluate the photocatalytic activity of  $\text{Mn}_3\text{O}_4$  nanoparticles,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  nanosheets and  $\text{MnO}_2$  nanoplates under visible light irradiation, the degradation of a model organic dye methylene blue (MB), was served for a probe reaction. As contrast, the experiments of MB degradation without photocatalysts in dark as well as under visible light irradiation were carried out. Besides, the MB removal with catalysts was mainly through simultaneous adsorption and degradation under illumination. Hence the adsorption experiments were also conducted in order to better study the photocatalytic performance of the photocatalysts. Before irradiation, The MB solution mixed with the catalysts were stirred for 30 min in dark to reach the absorption equilibrium. As can be seen from Fig. 6(a), the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell composite exhibited the highest catalytic activity under visible light irradiation, which significantly outperformed the pure  $\text{Mn}_3\text{O}_4$  and  $\text{MnO}_2$  catalysts. The adsorption efficiency of  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  were 11.1%, 31.0% and 36.5%, respectively. The higher adsorption capacity of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  might attribute to their higher surface area and more adsorp-

tion sites. In the contrast experiments, no MB was degraded in dark and 6.4% of MB was self-degraded under visible light irradiation for 1 h. After 1 h of visible light irradiation, 33.4%, 93.5% and 51.1% of MB dye could be degraded by  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  photocatalysts, respectively. In order to further investigate the degradation kinetics, the first-order kinetic model was applied to fit the degradation data and the fitting results were shown in Fig. 6(b). It was apparent that all experimental data followed the first-order kinetic model. The self-degradation rate constant of MB under visible light irradiation was  $0.0011 \text{ min}^{-1}$ , while the degradation rate constants of MB for  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  photocatalysts were 0.0068, 0.0456 and  $0.0119 \text{ min}^{-1}$ , respectively. Obviously, the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell composite exhibited the excellent activity under visible light irradiation, which was superior to the reported  $\text{MnO}_2/\text{TiO}_2$  and  $\text{Al}_2\text{O}_3\text{-Mn}_3\text{O}_4$  photocatalysts [25,37].

In general, the recyclability and stability are essential for the industrial applications of the photocatalysts. The MB degradation by  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell photocatalyst under visible light irradiation was carried out consecutively for five cycles. As shown in Fig. 6(c), the stable reusability of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  was observed since the removal efficiency of MB only decreased by 6.0% after five cycles. Besides, the concentrations of manganese in the reaction solutions were below the detection limit ( $0.5 \mu\text{g/L}$ ), indicating the stability of the  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  composite during the degradation process in aqueous solutions. The slight decrease of degradation efficiency with the increase in cycle might be resulted from the loss of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  in the regeneration process. Therefore, the stable and high-efficiency  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  core-shell photocatalyst would be an environment-friendly material with a bright application future in water treatment field.

### 3.4. Possible photocatalytic mechanism

Surface area of a nanomaterial is closely related to the number of adsorption sites as well as catalytic activities, which is an indispens-

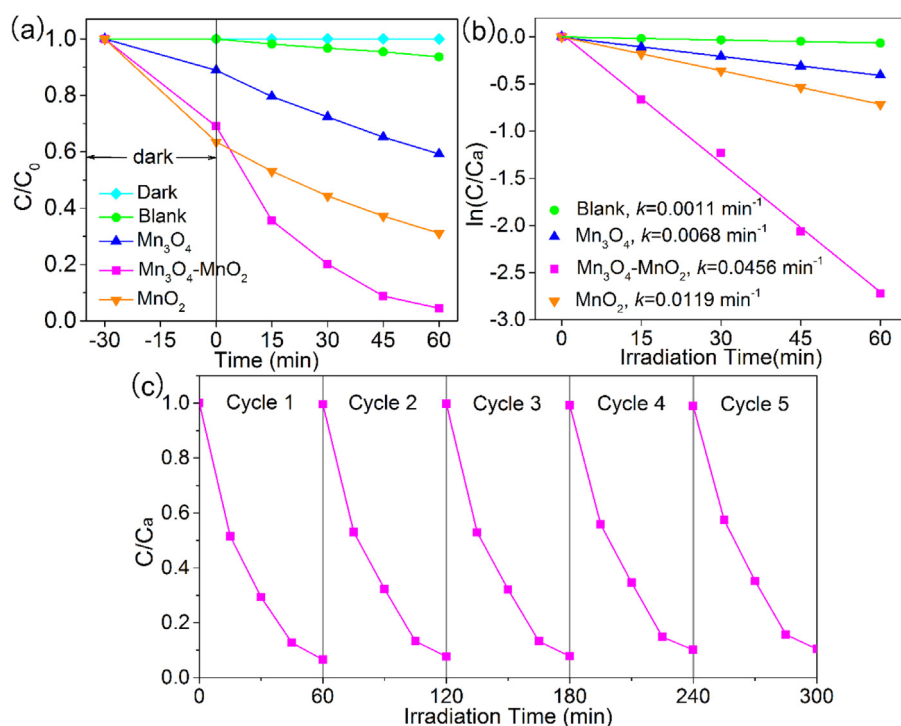


Fig. 6. (a) Photodegradation of MB by  $\text{Mn}_3\text{O}_4$ ,  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  and  $\text{MnO}_2$  and blank experiment; (b) Linear fit of experimental data by first-order kinetic model; (The  $C_0$  represents the MB concentration after stirring for 30 min in dark.) (c) Consecutive cycles of  $\text{Mn}_3\text{O}_4\text{-MnO}_2$  for MB degradation.

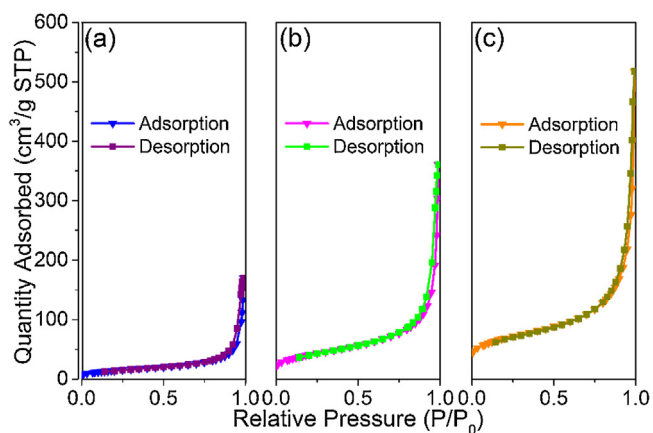


Fig. 7.  $N_2$  adsorption-desorption isotherms of (a)  $Mn_3O_4$  and (b)  $Mn_3O_4$ - $MnO_2$  and (c)  $MnO_2$ .

able factor in photocatalysis [22]. The Brunauer-Emmett-Teller (BET) surface area of  $Mn_3O_4$ ,  $Mn_3O_4$ - $MnO_2$  and  $MnO_2$  photocatalysts were measured by nitrogen ( $N_2$ ) adsorption-desorption method at 77 K. The  $N_2$  adsorption-desorption isotherms of the three samples were shown in Fig. 7. The adsorption isotherms belonged to type-IV classification [22]. The specific surface area (SSA) of  $Mn_3O_4$ ,  $Mn_3O_4$ - $MnO_2$  and  $MnO_2$  were calculated to be 51.8, 148.3 and 171.2  $m^2/g$ , respectively. The SSA of  $Mn_3O_4$ - $MnO_2$  core-shell nanosheets was significantly enhanced by doping  $MnO_2$ , which was almost three times higher than that of pure  $Mn_3O_4$ . The  $Mn_3O_4$ - $MnO_2$  with higher surface area could provide more activity sites, facilitating the photocatalytic process. The higher adsorption efficiency and degradation rate of  $Mn_3O_4$ - $MnO_2$  in Fig. 6(a) could partially attribute to its large surface area and more activity sites.

In order to analyze the light absorption property of  $Mn_3O_4$ ,  $Mn_3O_4$ - $MnO_2$  and  $MnO_2$  photocatalysts, the ultraviolet visible (UV-vis) diffuse reflectance spectra were measured and shown in Fig. 8A. The absorbance intensity of  $Mn_3O_4$  declined sharply when light wavelength was longer than 550 nm, corresponding to a band gap of 2.2 eV [22,24]. As can be seen from Fig. 8A (c), pure  $MnO_2$  showed a strong absorption in the ultraviolet and visible region, which was also observed in previous literature [25]. The  $Mn_3O_4$ - $MnO_2$  core-shell composite (Fig. 8A (b)) also had a strong absorption in the ultraviolet region as well as visible region. Clearly, it was  $MnO_2$  that significantly expanded the light absorption range of  $Mn_3O_4$ - $MnO_2$  composite, which was more photo-responsive than pure  $Mn_3O_4$ .

In order to further analyze the photocatalytic mechanism, the band structures of the pure  $Mn_3O_4$  and  $MnO_2$  were investigated. Firstly, the band gaps of the  $Mn_3O_4$  and  $MnO_2$  were acquired by employing the equation [15,16,22] below:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{n}{2}} \quad (8)$$

In the equation,  $\alpha$ ,  $h$  and  $\nu$  are absorption coefficient, Planck's constant and light frequency, respectively.  $E_g$  represents the band gap of a semiconductor and  $A$  is a proportionality constant. The values of  $n$  were 1 and 4 for direct transition semiconductors and indirect transition semiconductors, respectively. The value of  $n$  was 1 in this study as  $Mn_3O_4$  and  $MnO_2$  were both direct transition semiconductors [22,27]. Then the Eq. (8) could be expressed as Eq. (9) and the band gap ( $E_g$ ) of the  $Mn_3O_4$  and  $MnO_2$  could be obtained by linear extrapolation. The plots of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) for the pure  $Mn_3O_4$  and  $MnO_2$  were presented in Fig. 8B. It could be obtained that the band gaps of  $Mn_3O_4$  and  $MnO_2$  were 2.16 and 1.77 eV, respectively.

$$(\alpha h\nu)^2 = A^2(h\nu - E_g) \quad (9)$$

Table 1

Calculation of the band structure of the  $Mn_3O_4$  and  $MnO_2$ .

Sample	$E_g$ (eV)	$\chi$	$E_{CB}$ (eV)	$E_{VB}$ (eV)
$Mn_3O_4$	2.16	5.57	-0.01	2.15
$MnO_2$	1.77	5.96	0.57	2.34

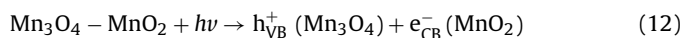
Secondly, the conduction band and valence band edges of the  $Mn_3O_4$  and  $MnO_2$  were estimated by the equations [22,38] below:

$$E_{CB} = \chi - E_e - \frac{1}{2}E_g \quad (10)$$

$$E_{VB} = E_{CB} + E_g \quad (11)$$

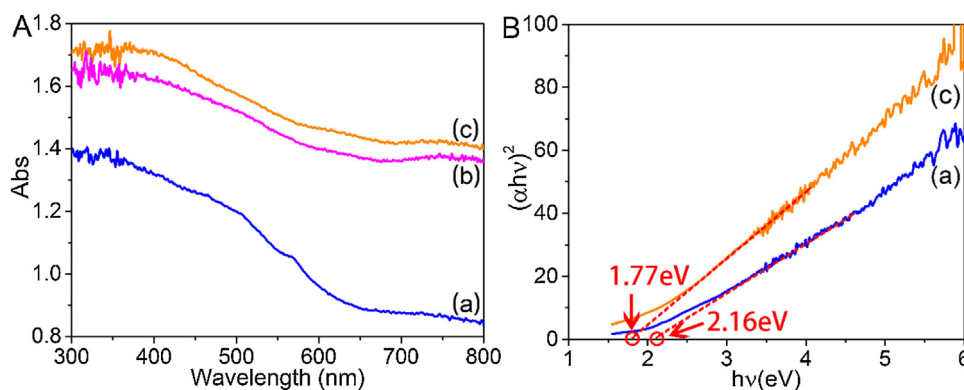
In the equations,  $E_{CB}$  and  $E_{VB}$  represent the conduction band edge and valence band edge, respectively.  $\chi$  is the absolute electronegativity of a semiconductor determined by the geometric average of constituent atoms.  $E_e$  is the free energy of electrons of the semiconductor on the hydrogen scale (about 4.5 eV). The band edge values of  $Mn_3O_4$  and  $MnO_2$  were summarized in Table 1. The conduction band and valence band edge values of  $Mn_3O_4$  were calculated to be -0.01 and 2.15 eV while the corresponding values of  $MnO_2$  were 0.57 and 2.34 eV, respectively.

Accordingly, the possible photocatalytic mechanism for the high-efficiency  $Mn_3O_4$ - $MnO_2$  core-shell composite was proposed and diagrammatized in Fig. 9. Interestingly, the band structure of  $Mn_3O_4$  and  $MnO_2$  showed a matching band position, forming a type-II heterojunction. The formation of type-II heterojunctions is considered as an effective means for photo-carriers separation, which can improve photocatalytic performance [19]. In this study, the photocatalytic property of  $Mn_3O_4$ - $MnO_2$  core-shell composite could be significantly enhanced by the separated electron-hole pairs. In addition, the core-shell structure of composite photocatalyst was also conducive to the enhancement of photocatalytic activity [15,28]. As displayed in Fig. 9, the conduction band (-0.01 eV) and valence band (2.15 eV) of  $Mn_3O_4$  were more negative than the conduction band (0.57 eV) and valence band (2.34 eV) of  $MnO_2$ , which was thermodynamically beneficial for the transfer of photo-generated charge carriers [19,22]. Under visible light irradiation, the electrons ( $e^-$ ) of  $Mn_3O_4$  were excited from valence band to conduction band, leaving holes ( $h^+$ ) in the valence band. Then the photo-induced electrons would transfer from the conduction band of  $Mn_3O_4$  to that of  $MnO_2$ . Thus, the photo-induced electrons would be enriched on  $MnO_2$  and the holes were reserved on  $Mn_3O_4$ , which effectively separated the photo-induced electrons and holes in space and prolonged the lifetime of carriers (Eq. (12)). Both the photo-induced holes and electrons were the dominant active centers for the visible light catalysis. The holes could react with hydroxyl ions, forming hydroxyl radicals in the valence band of  $Mn_3O_4$  (Eq. (13)). Meanwhile, the superoxide radical anions could be generated in the conduction band of  $MnO_2$  by interactions between the electrons and dissolved oxygen (Eq. (14)).

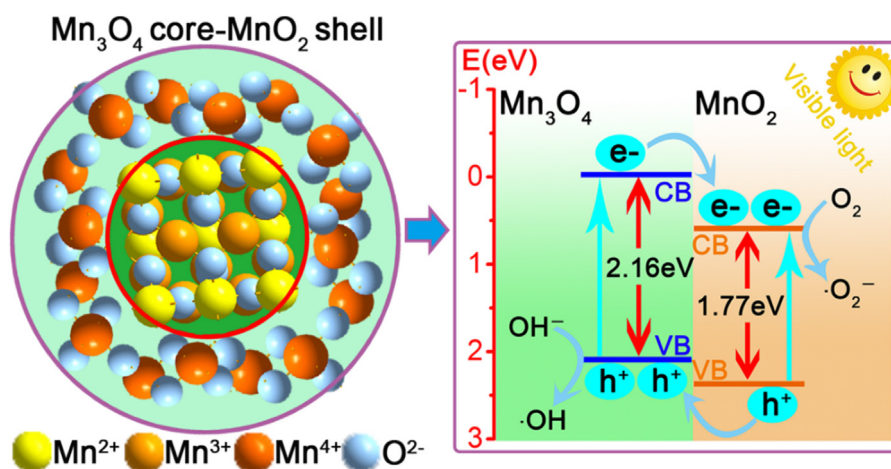


To further prove the efficient separation of photo-carriers in  $Mn_3O_4$ - $MnO_2$  composite photocatalyst, the transient photocurrent response and electrochemical impedance spectroscopy (EIS) of the samples were measured. As shown in Fig. 10A, the photocurrent of the three photocatalysts were stable under visible light, and the photocurrent sharply decreased as the lamp was turned off. Noticeably, the photocurrent of  $Mn_3O_4$ - $MnO_2$  was much higher than that of pure  $Mn_3O_4$  and  $MnO_2$ , indicating the effective separation and prolonged lifetime of charge carriers in  $Mn_3O_4$ - $MnO_2$  composite [15,39]. Besides, the charge transfer resistance at the

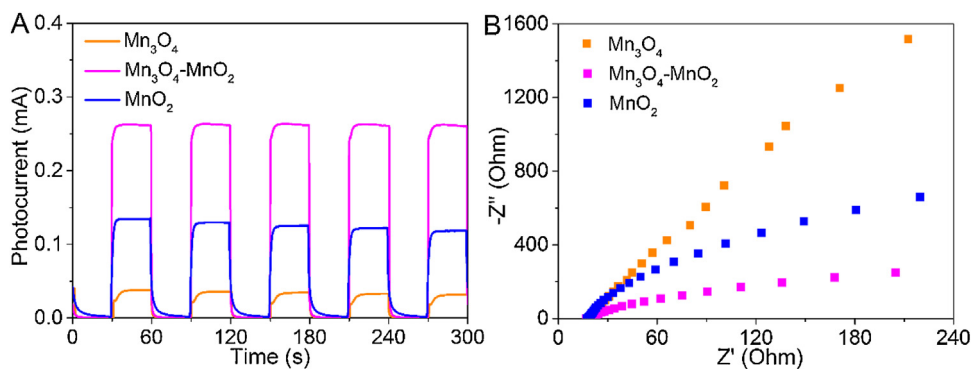




**Fig. 8.** (A) UV-vis diffuse reflectance spectra of (a) Mn<sub>3</sub>O<sub>4</sub>, (b) Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> and (c) MnO<sub>2</sub>; (B) Plots of  $(\alpha h\nu)^2$  versus photon energy ( $h\nu$ ) of (a) Mn<sub>3</sub>O<sub>4</sub> and (c) MnO<sub>2</sub>.



**Fig. 9.** Schematic interpretation of the photocatalytic mechanism for the high-efficiency Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> core-shell composite.



**Fig. 10.** (A) Transient photocurrent response of Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> and MnO<sub>2</sub> under visible light irradiation with light on/off cycles; (B) Electrochemical impedance spectroscopy of Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> and MnO<sub>2</sub> under visible light irradiation.

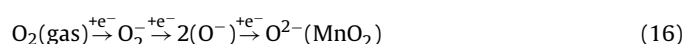
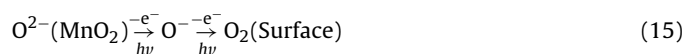
electrode/electrolyte interface was also analyzed. As is well known, a smaller diameter indicates a lower charge transfer resistance (i.e. more facile charge transfer) in Nyquist plots [15,39]. As shown in Fig. 10B, the Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> composite presented the smallest diameter among the three samples, indicating the lowest interfacial charge-transfer resistance. The higher charge separation and transfer efficiency of Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> composite enhanced the photocatalytic activity.

Moreover, the radical-trapping experiment showed that the superoxide radicals played the most vital role in the photo-degradation process, followed by the holes and hydroxyl radicals. Benzoquinone (BQ), disodium ethylenediamine tetraac-

etate (Na<sub>2</sub>EDTA) and *tert*-butyl alcohol (TBA) were employed as the probes of superoxide radicals, holes and hydroxyl radicals respectively [22] to identify the role of each active specie in the degradation process. As shown in Fig. S6, the removal efficiency of MB decreased from 93.5% to 47.0%, 61.3% and 69.1% respectively after adding the three scavengers to MB solution. Results indicated that superoxide radicals, holes and hydroxyl radicals were all played active parts in MB degradation, while the role of superoxide radicals was the most significant. Besides, the surface oxygen of Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> composite also made contributions to the formation of excited-state oxygen species during photocatalytic oxidation. The removal rate of MB with Mn<sub>3</sub>O<sub>4</sub>-MnO<sub>2</sub> photocatalyst decreased



by 34.2% in nitrogen atmosphere (supplied in Fig. S8A). The MB solution showed a definite degradation in the first 15 min under visible light irradiation, then the degradation rate became very slow. This was because the absorbed oxygen and bulk oxygen of amorphous  $\text{MnO}_2$  in turn formed active oxygen species with electrons at the early stage (Eqs. (14)–(15)) [32,40]. However, the movement of lattice oxygen from  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  to the surface normally needed thermal energy to overcome the large lattice energy, which could not form the active oxygen at room temperature in general [32]. The amount of active oxygen species dropped sharply in oxygen free conditions. Therefore, the degradation rate dramatically declined in the absence of atmospheric oxygen (Fig. S8A). Interestingly, the  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  core-shell composite still possessed high catalytic activity after five cycles in Fig. 6(c). Although the surface oxygen and the bulk oxygen were evolved, the oxygen vacancies on  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  surface would be replenished by dissolved oxygen in water (Eq. (16)) [32], which was further demonstrated in Fig. S8B in Supporting information. It can be inferred that the composite photocatalyst had strong self-regeneration capacity in air to maintain the outstanding catalytic performance.



#### 4. Conclusion

In summary, a novel  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  valence state heterojunction was fabricated by a facile and energy-effective hydrothermal method at 363 K. The XPS, XRD, SEM and TEM were used for characterization. Results showed that the  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  nanosheets with core-shell structure was composed of crystalline  $\text{Mn}_3\text{O}_4$  (tetragonal hausmannite) and amorphous  $\alpha$ - $\text{MnO}_2$ . In addition, the formation mechanism of the photocatalysts were discussed based on their composition and chemical stoichiometry. The specific surface area and visible light absorption of  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  composite were significantly enhanced by doping  $\text{MnO}_2$  compared to the pure  $\text{Mn}_3\text{O}_4$ . The  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  composite possessed the best photocatalytic activity with the removal efficiency of MB reaching 93.5% in 1 h under visible light irradiation. Further exploration of the mechanism indicated that the formation of the type II heterojunction in  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  composite might achieve the spatial separation of photo-induced carriers effectively. Moreover, the superoxide radicals played an important role in photo-degradation process, followed by the holes and hydroxyl radicals. The surface oxygen of  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  was also took part in the formation of active oxygen species. Besides, the  $\text{Mn}_3\text{O}_4$ - $\text{MnO}_2$  photocatalyst exhibited self-regeneration ability with atmospheric oxygen. These findings would provide a new perspective for manganese oxides applied in photocatalysis field.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.09.065>.

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